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Theoretical Study of Hydrotreating Process in Small Heterocyclic Rings

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A theoretical investigation has been made by use of DFT-B3lyp/cc-pvdz calculation levels, to clarify at the atomic scale of the hydrotreating process which depends on the removal of sulfur, nitrogen and oxygen atoms from the small heterocyclic rings such as thiirane, aziridine and oxyrane. Activation of C-S, C-N and C-O bonds has been done *via* a simple and a double protonation followed by a full optimization of geometry. Critical points on the potential energy surface, of the protonated systems, were located by use of the frequency calculation. Present results indicate that the small protonated heterocyclic rings have revealed a carbocationic system as organic reactive intermediates presented by a complex with a weak interaction. In addition, proton affinities and charge delocalizations based on NBO analysis have been taken to check the ability of the lone pair of heteroatoms to participate in the formation of H-S, H-N or H-O bonds.

Keywords: DFT, Hydrotreating processes, Carbocationic system, Small heterocyclic rings, NBO analysis.

INTRODUCTION

Hydrotreating processes [1-3] have the primary objectives to remove impurities, such as heteroatom and metal containing compounds, from a feedstock and to increase the hydrogen content of the feedstock [4]. The impurities of concern depend on the molecular weight of the feedstock being processed. Lower molecular weight feedstock such as naphtha, gasoline and diesel fuels have undesired impurities such as sulfur, nitrogen or oxygen containing compounds (S-compounds), (N-compounds) and (O-compounds) [5].

In general, the sulfur impurity is the major concern because S-compounds are often serious poisonous and inhibitors for other secondary upgrading process catalysts. Besides, they provoke environmental problems by the production of SOx, major sources of the air pollution [6,7]. The ease of removal of sulfur from a petroleum stream depends greatly on the structure of the sulfur compound being treated [8]. Generally, acyclic sulfur compounds such as thiols and disulfides are highly reactive and can be removes under very mild condition. However, compounds in which the sulfur atom is incorporated into a five-membered aromatic ring structure such as thiophene, are much less reactive and the reactivity decreases as the ring structure becomes increasingly condensed (one ring > two rings > three rings) [1].

Small heterocyclic rings (Fig. 1) are chosen to be investigated *via* a theoretical approach.

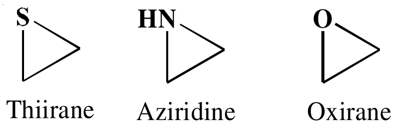

Fig. 1. Structures of small heterocyclic rings

The process of the hydrotreating which is based on the activation of C-X bonds (X = S, N, O) by a simple and double protonation of the small heterocyclic rings. We focused mainly on the geometry optimization of the protonated structures and their NBO analysis [9] to investigate the possible formation of H-X bonds. The interest of our work is to propose a description to clarify how the charge distribution in C-X bonds can explain the remove of sulfur, nitrogen and oxygen atoms as H_2S, NH_3 and H_2O, respectively.

COMPUTATIONAL METHODS

The DFT method [10] has been performed at B3lyp/cc-pvdz level using Gaussian03 software [11]. Full geometry optimizations were performed on each species without any symmetry constraint.

Each optimized structure was characterized by frequency calculations to be a minimum (without any imaginary vibrational frequency) or as transition structures (number of imaginary frequencies = 1). Results are described in Table-1.

NBO analysis [9] was also performed using B3lyp/cc-pvdz level to investigate charge delocalization and different

TABLE-1
ESSENTIAL PARAMETERS OF OBTAINING STRUCTURES (THE VALUES BETWEEN PARENTHESIS ARE THE DISTANCES C-X OF NONPROTONATED SYSTEMS)

Systems	E_T (uma)	ν_{min} (cm^{-1})	d (Å) C-X	d (Å) H-X	Symmetry
$C_2H_5S^+$	-477.073	-626.73	2.25(1.84)	1.37	Cs
$C_2H_6S^{++}$	-477.037	-849.97	2.31(1.84)	1.50	C_{2v}
$C_2H_5O^+$	-154.120	167.32	1.49(1.44)	2.06	C1
$C_2H_6O^{++}$	-154.086	-629.56	1.90(1.44)	0.99	Cs
$C_2H_6N^+$	-134.170	-1485.41	1.89(1.44)	1.02	Cs
$C_2H_7N^{++}$	-134.303	-403.88	1.89(1.47)	1.05	Cs

bonding character. Molecular figures are generated using Gauss View and ChemDraw Programs.

RESULTS AND DISCUSSION

Activation of thiirane: The protonation of the thiirane system (Fig. 2) generates two cations $C_2H_5S^+$ (Cs) and $C_2H_6S^{++}$ (C_{2v}). These structures are maxima on the potential energy surface. S1-C2 bond in $C_2H_5S^+$ cation is too long (2.25 Å) compared to the same bond in a thiirane molecule (1.84 Å). Besides, the C2-C3 bond is shortened and appears in this case with a distance 1.41 Å instead of 1.48 Å in the neutral system. However, S-H bond (1,37 Å) is comparable to the same one in the H_2S system (1.36 Å) which is estimated by the same level of calculation (Fig. 3).

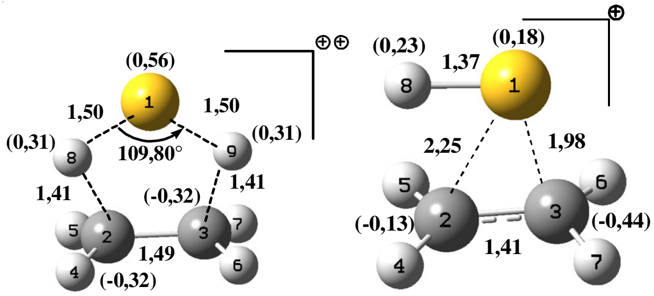

Fig. 2. Structures of ions $C_2H_5S^+$ and $C_2H_6S^{++}$

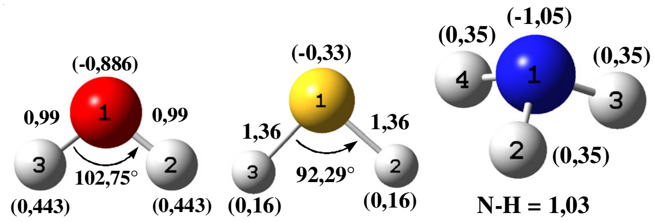

Fig. 3. Interatomic distances and charges of H_2S, NH_3, H_2O molecules

Activation of aziridine: The monoprotonated aziridine presented by the cation $C_2H_6N^+$ (Cs) which is obtained *via* the activation of N1-C2 bond (Fig. 4). The distance of this bond is 1,89 Å, which indicate the opening of the cycle and the capture of the proton H9 by nitrogen atom to form N1-H9 bond with an optimal distance (1.02 Å). The shortening of C2-C3 bond is characterized in this case by 1.41 Å instead of 1.48 Å in the aziridine system.

The aziridine that has undergone a double activation at the two bonds C-N gives the ion $C_2H_7N^{++}$(Cs) (Fig. 4). This ion presents an interaction between the ethylene (C2-C3 bond is nearly double (1.43 Å)) and the NH_3 molecule which lead in this case to the interaction ion-ion. The distances N-H are also of adequate values (1.05 Å).

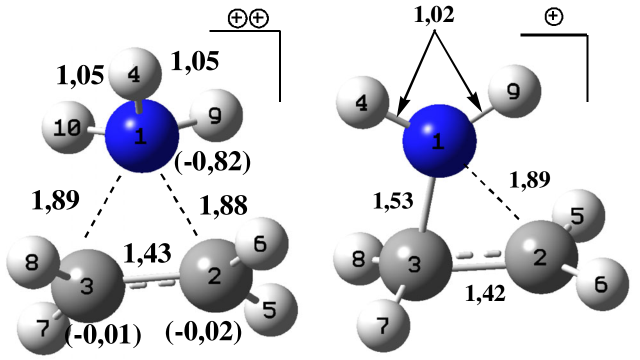

Fig. 4. Two ions $C_2H_6N^+$ and $C_2H_7N^{++}$

The cation $C_2H_5O^+$ (C_1) obtained by the protonation of O1-C2 bond, that leads to the opening of the cycle at the C2-C3 bond (Fig. 5). This bond became too long (2.39 Å). The cation $C_2H_5O^+$ present the capture of the proton added by the carbon instead of the oxygen, as well as the formation of a double bond O1=C3 of length 1.24 Å that presenting a stable system (minimum).

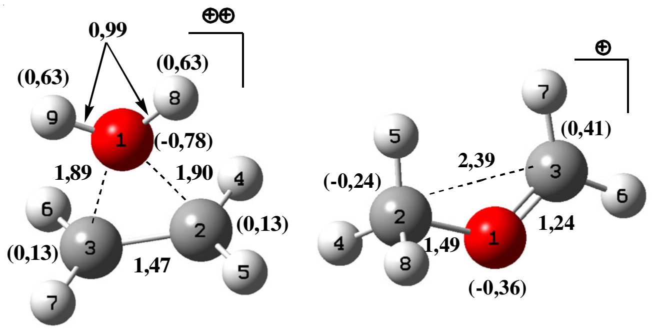

Fig. 5. Ions $C_2H_5O^+$ and $C_2H_6O^{++}$

On the other hand, the protonation of the two bonds O1-C2 and O1-C3 permissible to give a structure of which the C-O lengths C-O became 1.90 Å (instead of 1.44 Å) and the two protons are taken by the atom of oxygen while forming two O-H bonds with a distance of 0.99 Å [similar value to the O-H bond in the molecule of water (Fig. 3)]. In this case the system presents an interaction between two ions: H_2O with a total charge (+ 0.48) and C_2H_4 with a total charge (+1.52) (Fig. 5).

Each of optimized structure was characterized by frequency calculations to be a minimum (without any imaginary vibrational frequency) or as transition structures (number of imaginary frequencies = 1). Results are described in Table-1.

Charge delocalization in small protonated heterocyclic rings and NBO analysis: Delocalization of electron density between the filled (bonding or lone pair) Lewis type [12,13] NBOs and the empty (antibonding and Rydberg) non-Lewis NBOs leads to the transfer of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals (and thus, departure from the idealized Lewis structure description). It is referred to as 'delocalization' correction to the zeroth-order natural Lewis structure to a stabilizing donor-acceptor interaction. The energies of these interactions can be estimated by the second order perturbation theory [14].

In our previous work [15,16], we have investigated the activation of C-C explained by σ-donor character. In order to explore the electronic density of C-X bond in different protonated structures, we presented the occupation of the free pairs and H-X bonds as well as the electronic charge labeled the added proton in Table-2.

TABLE-2
ELECTRONIC VALUES OF H-X BONDS, LONE PAIRS OF X AND CHARGE OF ADDED PROTON

Systems	Values of lone pairs of X	Charge of added proton	Value of H-X bond
$C_2H_5S^+$	1.99; 1.92	0.23	1.85
$C_2H_6S^{++}$	1.98; 1.90; 0.88	0.31	–
$C_2H_5O^+$	1.96	0.26	–
$C_2H_6O^{++}$	1.99	0.63	(O1-H8) 1.98; (O1-H9) 1.95
$C_2H_6N^+$	1.97	0.46	1.95
$C_2H_7N^{++}$	–	H4 and H9 (0.52); H10 (0.54)	(N1-H4) 1.99; (N1-H9) 1.90; (N1-H10) 1.96

This investigation permitted us to value the elimination of the S, N and O heteroatoms by the way of the activation of C-X bonds and the following of the electronic occupation of free pairs and of bonds in which incorporate the heteroatom X. Table-3 describes the rate of occupations and the stabilization energy between the donor and the acceptor.

$C_2H_5S^+$ and $C_2H_6S^{++}$: The formation of the two free pairs of the sulfur atom in $C_2H_5S^+$ gives the following values: LP1 (1.99) and LP2 (1.92). It clearly shows that the atom of sulfur maintained relatively its electronic free pairs. The LP2 (1.92) does not participate completely in the formation of the S-H bond which present the value of (1.85). The origin of this value is mainly obtained through the charge distribution of the S1-C2 broken. This reflects the weak positive charge (0.23) labeled by the added proton. The main charge delocalization in this case occurs by the donation of S1-C3 and S1-H8 possessing the occupations 1.64 and 1.86 toward LP*(C2) with energies of 93.96 and 36.48 kcal/mol, respectively.

In the $C_2H_6S^{++}$ ion the two bonds C-S of the thiirane are activated and permit to distribute their electronic density on the set of atoms. The two protons acquired again of the electronic charge equal to (-0.69) and the atom of sulfur possesses in this case three electronic pairs (Table-3) LP1 = 1.98, LP2 = 1.90 and LP3 = 0.88. The charge delocalization of the three pairs (LP1, LP2 and LP3) is mainly oriented toward $LP^*(S1)$, $LP^*(S1)$ and $LP^*(C3)$ with energies of stabilization 20.41, 3.65 and 20.99 kcal/mol, respectively (Table-3).

$C_2H_5O^+$ and $C_2H_6O^{++}$: For the $C_2H_5O^+$ ion the proton taken by the carbon instead of the oxygen carries a small positive charge (+0.26). The delocalization of the charge produced on the free pair of the oxygen that remains, LP1(O1) (initial occupation rate 1.96), oriented mainly toward σ*C3-H7 with an energy of 6.63 kcal/mol. On the other hand the electronic density of the bond O1-C3 delocalized toward σ*C2-H8 and the energy in this case is 1,54 kcal/mol.

In the case of ion $C_2H_6O^{++}$, we observe the protonation of two bonds C-O of oxirane, the oxygen atom shows a free pair that remains intact (with an occupation of 1.99) and do not present any charge delocalization. The positive charge labeled the two hydrogens is relatively raised (0.63). The essential delocalization of electronic charge occurs in this case between O1-C3 with an occupation of 1.79 instead of 2 toward LP*C2 in which the energy of stabilization is 76.64 kcal/mol.

TABLE-3
NOTABLE ELECTRONIC CHARGE DELOCALIZATION IN ALL STRUCTURES

Structure	Donor	Value	Acceptor	E (kcal/mol)*
$C_2H_5S^+$	S1-C3	1.64	LP*(C2)	93.96
	S1-H8	1.86	LP*(C2)	36.48
	LP1(S1)	1.98	RY*(H8)	1.34
	LP2(S1)	1.92	σ*(S1-C3)	1.45
$C_2H_6S^{++}$	CR(S1)	2.00	LP*(S1)	5.17
	LP1(S1)	1.98	LP*(S1)	20.41
	LP1(S1)	1.98	RY*(C2)	0.34
	LP1(S1)	1.98	RY*(C3)	0.34
	LP2(S1)	1.90	LP*(S1)	3.65
	LP2(S1)	1.90	LP*(C2)	2.33
	LP2(S1)	1.90	LP*(C3)	2.33
	LP3(S1)	1.87	LP*(C2)	20.94
	LP3(S1)	1.87	LP*(C3)	20.99
	LP(H8)	0.68	RY*(S1)	4.14
	LP(H9)	0.68	RY*(S1)	4.14
$C_2H_5O^+$	LP1(O1)	1.96	σ*(C3-H7)	6.63
	C3-H6	1.98	σ*(O1-C2)	6.48
	LP1(O1)	1.96	RY*(C3)	2.65
	O1-C3	1.99	RY*(C2)	0.74
	O1-C3	1.99	σ*(C2-H8)	1.54
$C_2H_6O^{++}$	O1-C3	1.79	LP*C2	76;64
	O1-H8	1.98	LP*C2	11.88
	O1-H9	1.95	LP*C2	0.65
	C2-C3	1.99	LP*C2	3.08
$C_2H_6N^+$	N1-C3	1.83	LP*C2	61.45
	N1-C3	1.83	σ*(N1-H9)	01.09
	C2-C3	1.98	σ*(N1-H4)	05.04
	LP1(N1)	1.96	σ*(C3-H7)	04.33
$C_2H_7N^{++}$	N1-C2	1.62	LP*C3	114.75
	N1-H4	1.99	LP*C3	2.62
	N1-H9	1.94	LP*C3	1.89
	N1-H10	1.95	LP*C3	24.43
	C2-C3	1.99	LP*C3	6.26

*Only interactions with highest energy (strongest stabilization) are listed.

$C_2H_6N^+$ and $C_2H_7N^{++}$: Protonated N1-C2 bond of azeridine gives the structure of ($C_2H_6N^+$) in which the atom of nitrogen captures added proton to forming N1-H9 bond with an occupation of 1.95 and the charge labeled this proton is (+0.46). However, the free pair of nitrogen did not enter into the formation of this bond. Table-3 gives the value of this pair (1.97).

The ion $C_2H_7N^{++}$ do not present any free pair, nitrogen is tetra substituted N1-H4, N1-H9 N1-H10 and N1-C2 with occupations 1,99 1,94 1,95 and 1,62 respectively. The notable delocalization are of N1-C2 and N1-H10 toward LP*(C3) with energies of 114.75 and 24.43 kcal/mol.

Conclusions

Our theoretical study of hydrotreating of small heterocyclic rings focused mainly on the geometry optimization of the protonated structures. The added proton receives a density of electronic charge from different donors (lone pairs or/and σ-bonds) and leads to the opening of the rings by the formation of new bonds. The different cation geometries show that the protonation of C-S and C-N bonds lead in all cases to an elongation stretching toward a rupture. However, in case of oxirane protonation, generated ion $C_2H_5O^+$ evolves preferentially toward a rupture of the C-C bond instead of C-O bond. That indicates the strong delocalization of the charge density of σC-C bond compared to the lone pairs of the oxygen.

Charge delocalization analysis of these protonated rings gives an ordering of the participation of lone pairs: pair of N > pairs of O > pairs of S. Consequently, hydrotreating of these systems depend mainly of lone pairs of heteroatoms X to create H-X bonds. On the atomic scale, there is much explanatory information about the hydrotreating processes based on the spectroscopic analysis and serves to predict some results about the systems that containing five membered rings and more.

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